Theoretical Analyses of the Prewetting Supercritical Region

K. Omata
Faculty of Science and Technology
Keio University
Kawasaki 212-0058, Japan

We investigate the prewetting supercritical one-phase region by making use of the Monte Carlo simulations and the density functional theory. We deal with Lennard-Jones (LJ) systems in which the fluid-fluid and fluid-substrate interactions are given by the LJ 12-6 and LJ 9-3 potentials, respectively. After the prewetting line is determined in the pressure (P)—temperature (T) plane or the temperature—density (ρ) plane of the phase diagram, the prewetting supercritical region is identified. Then, we calculate the two-dimensional (2D) static structure factor SQ defined in a first adsorption layer. The analyses of SQ characterize the prewetting supercritical region as follows. First, the enhancement of SQ in the small q region is fitted to the function of the Ornstein-Zernike form, where q is a wave number. The extrapolation derives the q = 0 component of SQ, which is proportional to the 2D compressibility, and the locus of the maxima in the compressibility provides a line in the P--T phase diagram. It is shown that the slope of this line differs from that of the prewetting line, and they meet at the prewetting critical point. This feature is in good agreement with the experimental results of the helium-on-cesium system, and in particular, the mercury-on-sapphire system.

Secondly, we study the other parameter XI included in the Ornstein-Zernike function, which describes the 2D correlation length. When the locus of the XI maxima is added to the P--T phase diagram, the resulting line is located in the higher pressure region above the locus of the compressibility maxima, implying that a wetting film grows in two stages with increasing pressure. While this work focuses on static properties, the behavior is reminiscent of the two-stage process in the spinodal decomposition.

Thirdly, we analyze the Fisher--Widom (FW) line on which the pairwise correlation function exhibits a crossover between the motonic and oscillatory decay. The feature of the decay is reflected in the large q region of SQ, and characterized appropriately by the magnitude of SQ estimated at the first-peak position q_1. By identifying the temperature and pressure at which SQ(q_1) increases the most rapidly, the FW line is determined in the phase diagrams. This line is expected to indicate the entropy change in the prewetting supercritical region.